

Studies on AB₅ Metal Hydride Alloys with Sn Additives

B. V. Ratnakumar, S. Surampudi, S. DiStefano and G. Halpert
Energy Storage Systems Group, Jet Propulsion Laboratory
4800, Oak Grove 1A., Pasadena, California 91109

and
C. Witham and B. Fultz

Division of Engineering & Applied Science
California Institute of Technology, Pasadena, California 91125

Introduction

The use of metal hydrides as negative electrodes in alkaline rechargeable cells is becoming increasingly popular, due to several advantages offered by these metal hydrides over conventional anode materials (such as Zn, Cd) in terms of specific energy, environmental cycle life, and compatibility. Besides, the similarities in the cell voltage, pressure characteristics and charge control methods of the Ni-MH cells to the commonly used Ni-Cd point to a projected take over of 25% of the Ni-Cd market for consumer electronics by the Ni-MH cells in the next couple of years.

Two classes of metal hydride alloys based on rare earth metals (Al₁₃)^(1,2) and titanium (AB₅)⁽³⁾ are being currently developed at various laboratories. AB₅ alloys exhibit higher specific energy than the AB₁₃ alloys but the state of the art commercial Ni-MH cells are predominantly manufactured using AB₅ alloys. The AB₅ alloys are essentially based on LaNi₅ with various substituents for La as well as Ni to stabilize the alloy during charge-discharge cycling, by reducing the internal stress on hydrogen absorption and/or forming protective surface films. For example, the volume expansion in the unit cell is reduced by a partial substitution of Ni with Co and the interfacial properties improved with small amounts of Al or Si⁽⁴⁾. Sakai et al⁽⁴⁾ studied the ternary alloys with different ternary solutes including Mn, Cr, Al, Co and Cu. The cycle life improves upon the substitution of Ni with the ternary solute in the order Mn < Ni < Cu < Cr < Al < Co. A substitution of the rare earth metal site with Ti⁽⁵⁾, Zr⁽⁶⁾, or other lanthanides such as Nd⁽¹⁾ and Ce⁽⁷⁾ may promote the formation of a protective surface film and enhance the cycle life. This eventually led to the use of relatively inexpensive mischmetal, Mn (a naturally occurring mixture of rare earth metals La, Ce, Pr and Nd) for La in the alloy formulations such as (Mn)(Ni-Co-Mn-Al)₅^(8,9).

In general, the beneficial effect of the substituents for either La or Ni is accompanied by an undesirable decrease in the hydrogen absorption capacity, long activation and slow kinetics of hydrogen absorption and desorption. In our recent communication⁽¹⁰⁾, we described the advantages associated with Sn as a ternary additive. The addition of small amounts (3.5 at%) of Sn improves the cycle life, with marginal reduction in the specific capacity and no reduction in the kinetics of absorption and desorption. In this paper, we will compare the properties of La-Ni-Sn alloys to the MnNi₅-based alloys, present further studies on the Sn-modified AB₅ alloys of differing Sn contents and report the effect of overcharge on the cycle life.

Experimental

The LaNi₅-XSrX alloys were prepared in an arc-melting furnace and annealed in vacuum at 950°C for 72 hours. The alloys were then crushed to 10 mesh in an argon glove box, followed by several hydrogen absorption-desorption cycles to optimize the powder surface area. The fine alloy powder (<75 μm) was mixed with 19% conductive diluent, i.e. NiCO nickel powder (1 μm), and 5% Teflon binder. The electrodes were fabricated by hot-pressing the mixture onto an expanded Ni screen. The electrodes for the basic electrochemical studies were fabricated by filling the BAS disk electrodes with electrode powders of equal quantities to ensure consistent values for the electrode area (0.17 cm²) and porosity. The Ni-MH test cells (~250 mAh) contained excess positive electrode (NiOOH), excess electrolyte (3.1% KOH), and a HgO/Hg reference electrode. Cycling of the cells was carried out using an in-house automatic battery cycler at constant current (4 mA/cm², C/5 rate) to a cut off voltage of 0.5 V vs. the reference electrode during discharge and to a fixed charge return. DC polarization experiments were performed using an EG&G 273 Galvanostat/Potentiostat interfaced to an IBM-PC.

Results and Discussions

The pressure-composition isotherms obtained from the gas phase studies as well as the electrochemical isotherms indicate that the equilibrium pressure of LaNi₅ during hydrogen absorption decreases upon the substitution of small amounts of Ni with Sn. Accordingly, the chargeability of the MH electrode in the present cell configuration is expected to improve in the Sn-modified alloys. Indeed, the specific capacity of the Sn modified alloys obtained from the charge-discharge tests is high both in the flooded cell and prismatic configuration and is in the range of 275-300 mAh/g (Fig. 1). This is noticeably higher than even some of the state-of-the-art, mischmetal based, AB₅ MH alloys evaluated at JPL.

Further, the capacity retention during charge-discharge cycling is vastly improved upon the addition of Sn; the capacity after 75 cycles is well over 2(K) mAh/g. Such improvement in the cycle life upon Sn addition was also observed with multi-component alloys⁽¹¹⁾. We have preliminary evidence that the cycle life is dependent on the extent of overcharge. The capacity after 75 cycles is higher in the cell subjected to 115% charge return, as compared to 125% charge return (Fig. 2). The evolution of hydrogen during overcharge might be causing a shedding of the electrode material by erosion. Despite the fact the Ni-MH sealed contains excess negative capacity to prevent such hydrogen evolution at the negative, this may occur in the later stages of cycling.

In addition to improvements in the initial capacity and capacity retention, the addition of Sn has caused no problems related to activation and kinetics. Instead, the alloy exhibited a high initial capacity in the first discharge (Fig. 2) and also faster kinetics (Fig. 3). The polarization resistance obtained from DC polarization experiments reveal a low value for the Sn-modified alloy as compared to either the binary alloy or even some of the state of the art mischmetal based AB₅ alloys evaluated at JPL. The improved kinetics for hydrogen absorption/desorption processes at the Sn-modified MH electrode are evident also from the high discharge capacities obtained at C/2 rate (175 mA/cm²) as compared to the C/5 rate (4 mA/cm²) used for the multi-

component alloys. The high discharge voltages of Sn-containing alloys during anodic polarization (discharge) of MH disk electrodes further illustrate the improved kinetics at the MH electrode upon the addition of Sn.

Studies are currently underway to determine the Sn content in the MH alloy that will optimize the cycle life, specific capacity and kinetics of absorption and desorption. We are also examining the beneficial effect of Sn when misch metal is substituted for 1a, the composition of the misch metal having been optimized in our earlier studies on various AB_5 -M alloys⁽¹²⁾. Other aspects related to the oxidative stability of the MH alloys and the diffusivity of hydrogen in the MH alloys are being examined in the Sn-modified alloys and compared with results from various AB_5 MH alloys.

Acknowledgments

This work was carried out at the Jet Propulsion Laboratory under contract with the National Aeronautics and Space Administration and at the California Institute of Technology with the assistance of NSF grant DMR-9213447. Gratitude is extended to Dr. Bob Bowman of Aerojet Corp. for providing the alloys tested here.

References

1. J. G. (i. Willems, *Philips J. Res.*, 39 (Suppl. 1), 1 (1984); J. G. Willems and K. H. J. Buschow, *J. Less Common Metals*, 129, 13 (1987).
2. T. Sakai, K. Muta, H. Miyamura, N. Kuriyama and H. Ishikawa, *Proc. Symp. Hydrogen Storage Materials: Batteries and Electrochemistry*, ECS Pre. Vol. 92-5, p. 59 (1992); T. Sakai, H. Yoshinaga, H. Miyamura and H. Ishikawa, *J. Alloys and Compounds*, 180, 37 (1992).
3. S. R. Ovshinsky, M. A. Fetecenko and J. Ross, *Science*, 260, 176 (1993); M. A. Fetecenko, S. Venkatesan and S. R. Ovshinsky, *Proc. Symp. Hydrogen Storage Materials: Batteries and Electrochemistry*, ECS Pre. Vol. 92-5, p. 141 (1992); M. A. Fetecenko, S. Venkatesan, K. C. Hong and B. Reichman, *Power Sources*, Vol. 12, p. 411 (1985).
4. T. Sakai, K. Oguro, H. Miyamura, N. Kuriyama, A. Kato and H. Ishikawa, *J. Less-Common Metals*, 161, 193 (1990).
5. T. Sakai, H. Miyamura, N. Kuriyama, A. Kato, K. Oguro and H. Ishikawa, *J. Less-Common Metals*, 159, 127 (1990).
6. T. Sakai, H. Miyamura, N. Kuriyama, A. Kato, K. Oguro and H. Ishikawa, *J. Electrochem. Soc.*, 137, 795 (1990).
7. T. Sakai, T. Hazama, H. Miyamura, N. Kuriyama, A. Kato and H. Ishikawa, *J. Less-Common Metals*, 172-174, 1175 (1991).
8. N. Furukawa et al (Sanyo Electric Co.), *Proc. IBA Meeting*, Seattle, WA, Oct. 12-13 (1990).
9. I. Matsumoto and A. Ohita (Matsushita, Japan), *Proc. IBA Meeting*, Seattle, WA, Oct. 12-13 (1990).
10. B. V. Ratnakumar, G. Halpert, C. Witham and B. Fultz, *J. Electrochem. Soc.*, (in press).
11. A. Anani, A. Visintin, K. Petrov and S. Srinivasan, *J. Power Sources*, 47, 261 (1994).
12. B. V. Ratnakumar, S. Surampudi, S. DiStefano and G. Halpert, *Proc. 76th IOWC Sources Conf.*, Cherry Hill, NJ, June 6-9 (1994).

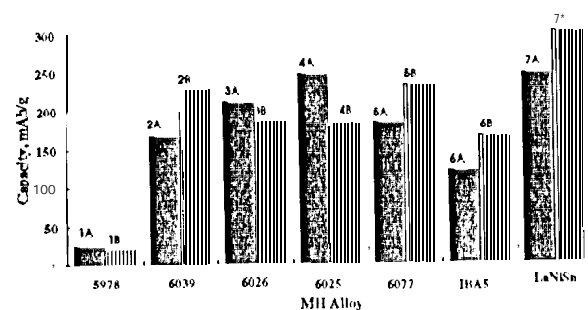


Fig. 1: Comparison of the specific capacities in A) flooded cells and B) prismatic cell configurations, of 1) binary $1aNi_5$ and the state-of-the-art misch metal based, AB_5 MH alloys (2-6) and 7) $1aNi_{4.8}Sn_{0.2}$.

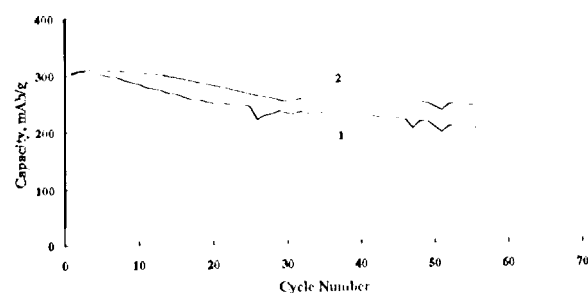


Fig. 2: Variation of the specific capacity of 250 mAh, negative-limited cells containing $1aNi_{4.8}Sn_{0.2}$ MH alloy, at C/2 rate (12 mA/cm²) to 0.5 V vs. Hg/HgO on discharge and to 1) 125% and 2) 115% charge return.

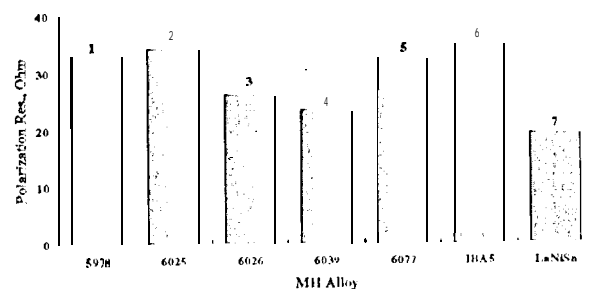


Fig. 3: Comparison of polarization resistance from DC micropolarization studies, of 1) binary $1aNi_5$ and the state-of-the-art misch metal based, AB_5 MH alloys (2-6) and 7) $1aNi_{4.8}Sn_{0.2}$.

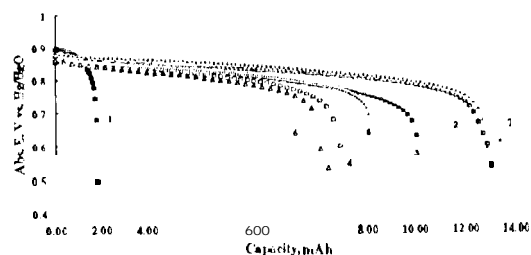


Fig. 4: Comparison of discharge curves at 50 mA/cm² of 1) binary $1aNi_5$ and the state-of-the-art misch metal based, AB_5 MH alloy disk electrodes (2-6) with 7) $1aNi_{4.8}Sn_{0.2}$.